

**REMARKS**

By the present Amendment, claims 1 and 6-17 are pending in the application. The Preliminary Amendment is submitted to place the specification and claims in better form for examination by the U.S. Patent and Trademark Office.

It is requested that the undersigned be contacted so to address any issues raised by this amendment or this application and that prosecution of the instant application expedited.

Respectfully submitted,

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## SURFACE MODIFIED STAINLESS STEEL

### RELATED APPLICATION DATA

[0001] This application is a §371 National Stage Application of PCT International Application No. PCT/SE2003/001159 filed July 2, 2003, which International Application was published by the International Bureau in English on January 15, 2004, the entire contents of which are incorporated herein by reference. This application also claims priority under 35 U.S.C. §119 and/or §365 to Swedish Application No. 0202107-9, filed July 3, 2002, the entire contents of which are incorporated herein by reference.

### FIELD OF THE INVENTION DISCLOSURE

[0002] The present invention disclosure relates to a stainless steel, which after nitriding exhibits a hardened surface layer with a hardness of at least 1200 Hv and which. Such stainless steel is particularly useful, for example, in applications with high demands on a combination of high strength and/or toughness and wear resistance and as a substrate for coating.

### BACKGROUND OF THE INVENTION STATE OF THE ART

[0003] In the discussion of the state of the art that follows, reference is made to certain structures and/or methods. However, the following references should not be construed as an admission that these structures and/or methods constitute prior art. Applicant expressly reserves the right to demonstrate that such structures and/or methods do not qualify as prior art against the present invention.

**COMPARISON DOCUMENT**

**[0004]** Stainless steel alloys are relatively less hard than other steel materials. As a result, in many applications the stainless steel article or part is provided with a hardened surface, often referred to as case hardening. The concept of case hardening is to transform a relatively thin layer of material at the surface of the part by enrichment of carbon or other ingredients to make the surface harder than the matrix of the alloy, ~~where matrix is the of the surface modification unaffected part of the steel.~~ The steel thus retains in bulk the desired formality of stainless steel without the softness of the matrix at the ~~surface of~~ modified steel surface.

**[0005]** Stainless steels are often casehardened by carburization. Carburization is a process by which carbon atoms are diffused in solution into the surface of the article. Known case hardening processes are performed at high temperatures. However, carburization processes performed at temperatures greater than about 540°C (for stainless steel alloys) can promote the formation of carbides in the hardened surface.

**[0006]** Plasma nitriding is an alternative case-hardening process, ~~which~~. Plasma nitriding is carried out in a glow discharge in a nitrogen gas-containing mixture at a pressure of 100 to 1000 Pa (1 to 10 mbar), ~~is one of the used.~~ This method to treat treats stainless steel surfaces, resulting in a nitrogen diffusion layer having high hardness and excellent wear resistance. Nitriding hardening is induced by the precipitation of nitrides in the surface layer.

~~DESCRIPTION OF THE RELATED ART~~

**[0007]** Plasma nitriding is ~~the most a~~ recently developed surface hardening procedure. The process ~~replaces~~ can replace traditional nitriding methods, such as gas nitriding ~~and nitrocarburization~~ and nitrocarburization (short-term gas nitriding, bath nitriding and tenifer treatment) as ~~identical~~ similar thermo-chemical conditions can be established in this process. Plasma nitriding achieves higher hardness and wear resistance, while creating lower distortion.

**[0008]** Plasma nitriding is very cost effective. This is due to the fact that subsequent machining, finishing and residue-removal processes are frequently not required. Similarly, supplementary protective measures, such as burnishing, phosphatizing, etc., under some conditions even galvanizing and hard-chrome plating, may not be necessary.

**[0009]** Plasma nitriding is performed in a vacuum furnace. Treatment temperatures in the range of 400 to 580°C are employed subject to the requirements of the process at hand. Typical treatment temperatures are in the range of 420 to 500-~~C~~ °C. ~~The most commonly~~ Commonly used process gases are ammonia, nitrogen, methane, and hydrogen. Oxygen and carbon dioxide are used in the ~~corrosion protective~~ corrosion protective step of post-oxidation. Aside from the type of process gas used, pressure, temperature, and time are the main parameters of the treatment process. By varying these parameters, the plasma nitriding process can be ~~finetuned~~ fine tuned to achieve the exact desired properties in any treated component.

**[0010]** Any iron-based material can be subjected to plasma nitriding. The process does not require the use of special types of nitriding steel. The

results achieved through plasma nitriding can be accurately reproduced with ~~pinpoint accuracy~~. This is especially important in the manufacture of serial products. US ~~5,632,826~~ 5,632,826 discloses a precipitation hardened martensitic alloy in which the strengthening is based on the precipitation of particles. The strengthening particles have a quasicrystalline structure, said structure being essentially obtained at aging times up to 1000 h and tempering treatments up to 650 °C. This strengthening involves an increase in tensile strength of at least 200 MPa. It has now surprisingly been found that if steel according to US ~~5,632,826~~ 5,632,826 is nitrided on the surface, an unexpected further increase in surface hardness is obtained ~~in difference~~ compared to the matrix of said stainless steel.

#### SUMMARY OF THE INVENTION

**[0011]** An exemplary embodiment of a stainless steel comprises a composition (in weight-%):

Carbon            max 0.1

Nitrogen        max 0.1

Copper           0.5 to 4

Chromium        10 to 14

Molybdenum     0.5 to 6

Nickel            7 to 11

Cobalt           0 to 9

Tantalum        max 0.1

Niobium         max 0.1

Vanadium    max 0.1

Tungsten    max 0.1

Aluminum    0.05 to 0. 6

Titanium    0.4 to 1. 4

Silicon       max 0.7

Manganese ≤ 1. 0

Iron    balance and

normally occurring usual steelmaking additions and impurities, wherein said stainless steel after nitriding exhibits a hardened surface layer with a hardness of at least 1200 Hv.

**[0012]** An exemplary method for making a surface modified stainless steel comprises subjecting a stainless steel to a nitriding process at a temperature of 450 to 580°C for a time period of 1 to 40 hours in a plasma nitriding atmosphere, the stainless steel having a composition comprising:

Carbon       max 0.1

Nitrogen    max 0.1

Copper       0.5 to 4

Chromium    10 to 14

Molybdenum       0.5 to 6

Nickel       7 to 11

Cobalt       0 to 9

Tantalum    max 0.1

Niobium    max 0.1

Vanadium    max 0.1

Tungsten      max 0.1

Aluminum      0.05 to 0.6

Titanium      0.4 to 1.4

Silicon          max 0.7

Manganese  $\leq$  1.0

Iron      balance and

normally occurring usual steelmaking additions and impurities.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0013]** The following detailed description of preferred embodiments can be read in connection with the accompanying drawings in which like numerals designate like elements and in which:

**[0014]** FIG. 1 is a light-optical micrograph showing the microstructure of an exemplary embodiment of the surface modified stainless steel in 500X, where A is the nitrided surface layer and B is the stainless steel matrix.

**[0015]** FIG. 2 is a graph showing the hardness (in Hv) plotted over the depth (in mm) from the surface.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

**[0016]** ~~It is therefore a primary object of the present invention to provide a~~  
A stainless steel alloy characterized by increased hardness at the surface of  
said alloy after modification of the surface at the same time as the hardness  
of the matrix of the stainless steel is also increased. ~~Another object of the~~

~~invention is to provide~~ is provided. In addition, products made of said surface modified stainless steel. ~~An additional object of the present invention is to provide~~ are provided. Further, a stainless steel substrate for coating with wear resistant layers is provided.

#### ~~BRIEF DESCRIPTION OF THE DRAWINGS~~

Fig. 1 ~~shows a light optical micrograph of the microstructure of one sample of the surface modified stainless steel according to the present invention in 500X, where A is the nitrided surface layer, B is the stainless steel matrix.~~

Fig. 2 ~~shows the hardness (in Hv) plotted over the depth (in mm) from the surface.~~

#### ~~DETAILED DESCRIPTION OF THE INVENTION~~

**[0017]** In exemplary embodiments, the The stainless steel substrate before surface modification ~~according to the present invention~~ has the following composition (in weight-%):

Carbon	max 0.1
Nitrogen	max 0.1
Copper	0.5- <u>to</u> 4
Chromium	10- <u>to</u> 14
Molybdenum	0.5- <u>to</u> 6
Nickel	7- <u>to</u> 11
Cobalt	0- <u>to</u> 9
Tantalum	max 0.1



Niobium	max 0.1
Vanadium	max 0.1
Tungsten	max 0.1
Aluminum	0.05- <u>to</u> 0. 6
Titanium	0.4- <u>to</u> 1. 4
Silicon	max 0.7
Manganese	$\leq$ 1. 0
Iron	balance

and normally occurring usual steelmaking additions and impurities.

**[0018]** Said stainless steel contains quasicrystalline particles in the martensitic microstructure as a result of a precipitation hardening.

**[0019]** Plasma nitriding is a surface hardening process, which utilizes the properties of gas plasma, i.e., an ionized gas, to achieve desirable mechanical properties at the surface of the work piece. The main influential parameters in nitriding are pressure, temperature, and time of treatment as well as the chemical composition of the ionized process gas. Plasma nitriding typically takes place at a vacuum pressure between 0.3 to 10 mbar. The actual treatment pressure chosen is governed by the geometry of the part and the desired surface layer structure.

**[0020]** The treatment temperature in the range of 400 to 580 °C is selected according to the type of material and pre-treatment of the part and the desired layer structure. Treatment time varies between 10 minutes and 70 hours, and depends on the part to be treated as well as the desired structure and thickness of the layers formed. Plasma nitriding uses ammonia or gas

mixtures containing methane, nitrogen, and hydrogen as the process gas.

The process gas used is selected subject to the nature of the part to be treated and the required layer structure.

**[0021]** In exemplary embodiments, ~~The invention also relates to~~ a material treated with the disclosed method ~~according to the present invention in~~ can be in the form of wire, plate, strip, tube and pipe and other geometries, especially complex geometries for use in applications with high demands on a combination of high strength and/or toughness and wear resistance, such as, e. g., wear parts of engines and other engine components, impact loads, such as safety devices, cam followers, cam follower pads, valve stems, valve stem guides, piston pins, piston shafts, hydraulic pistons, ejector pins, safety protection plates, lock cylinders and other locking devices, blocking elements, thief-proof equipment or the like.

**[0022]** EXAMPLE The1: A stainless steel substrate as described earlier herein was subjected to a surface modification by a plasma nitriding process at 450 to 580 °C during a period of time of 1 to 40 hours. This process obtains a hardening of the surface between 0.05 and 0.5 mm. The hardening process can be carried out on wire, plate, strip, tube and pipe and parts with a wide variation of geometries, especially complex geometries. It is a special advantage of the stainless steel substrate used according to the ~~present invention~~ disclosed process, that very complex geometries can be formed without any changes in dimension. The hardness of the surface is at

least twice the hardness of the substrate 0.5 mm into the matrix. ~~It is at~~ The hardness of the surface is 1200 Hv, preferably alternatively at least 1100 Hv.

**[0023]** ~~Figure 1 illustrates~~ 2 is a graph illustrating the hardness profile from the surface of the ~~substrates~~ substrate into the matrix. ~~It has unexpectedly shown~~ shows that the hardening effect is visible down to about 0.5 mm into the matrix. It is therefore considered ~~being a~~ big advantage of this combination of substrate and the method of surface treatment, that creates a surface modified material with a deep-hardened surface zone.

**[0024]** ~~Thus,~~ Exemplary embodiments of the surface modified stainless steel according to the present invention is particularly well suited for use as substrate for the deposition of a wear resistant coating.